

MECHANISM OF SUCCESSIVE SOLVOLYTIC EXTRACTION OF COAL

D. K. Sharma and S. K. Singh
Centre for Energy Studies,
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi-110016, INDIA

KEYWORDS: Coal, Extraction, Solvents

Coal macromolecules are associated (interlocked and intermeshed) with each other so strongly that it generally requires stronger conditions for extraction or solubilization of more than 10-20% of coal. Extraction of coal in an organic solvent is an essential requirement for the conversion of coal to value added fuels and chemicals without a significant loss in original coal constitution and its energy. As a part of our large program on development of convenient and cost effective techniques for solvent extraction of coal under atmospheric pressure conditions using coal derived chemicals, work on successive extraction of coal using anthracene oil-quinoline (Qn) - liquid paraffin (LP) and anthracene oil (AO) - ethylenediamine (EDA) - liquid paraffin was undertaken. The procedure for the successive extraction of coal using different solvents for 24h extraction, has been reported earlier (1). In fact, Assam coal, Talcher coal and Neyveli lignite (analysis shown in Table 1) when subjected to successive solvent extraction (for 24h in each solvent), i.e., anthracene oil-ethylenediamine-liquid paraffin solvents showed 70% extraction of Assam coal, 59% extraction of Talcher coal, and 63% of Neyveli lignite. This was more than that observed using AO-Qn-LP solvents in successive extractions (Table-2) (1).

Table - 1: Analysis of Coals and Lignite

Proximate Analysis: On Dry Basis (%)

Coal	Moisture	Mineral Matter	Volatile Matter	Fixed Carbon
Assam Coal	2.8	8.3	42.0	46.9
Talcher Coal	2.1	16.9	38.8	42.2
Neyveli Lignite	8.7	6.1	46.6	38.6

Ultimate Analysis (% on Dry Mineral Matter Free Basis)

Coal	Carbon	Hydrogen	Sulfur	Nitrogen	Oxygen	Atomic H/C	O/C
Assam Coal	77.0	5.7	3.8	1.5	12.0	0.88	0.12
Talcher Coal	74.8	5.3	1.0	1.6	17.3	0.87	0.17
Neyveli-Lignite	62.0	5.3	1.4	0.9	30.4	1.02	0.37

The observations showed that there are solvents which are capable of successively extracting coal resulting in 60-70% extraction of coal. In fact, maximum extraction of Assam coal was found to be in AO and this was 36%. This showed that a major portion of coal (64%) remains unextracted. The reason for this could be that the concentration gradient created by AO inside the solid coal and outside in the coal extract reaches a saturation stage and further

extraction in AO is not possible. This is the limit to which coal molecules can be associated with AO. Some of AO also gets into solid coal that is, it gets dissolved in coal. This mutual solubility is because of the reason that like dissolves like, as the major part of macromolecular and polyaromatic heterogeneous structure of coal resembles that of the constituents present in AO, especially phenanthrene and carbazole.

Table - 2: Successive Solvolytic Extraction of Coals Using AO-EDA-LP and AO-Qn-LP Solvent Systems

Coal Sample	Extractability (%)				Total Extraction Yield	
	AO	EDA	QN	LP	On Original Coal Wt. Basis	On DMMF Basis
Assam Coal	33	26	*	28	65	70
Assam Coal	33	*	23	22	60	65
Talcher Coal	22	25	*	10	48	59
Talcher Coal	22	*	15	9	40	48
Neyveli Lignite	30	30	*	21	61	63
Neyveli Lignite	30	*	22	23	58	60

* This particular solvent was not used in the successive extraction
DMMF - Dry mineral matter free
Wt. - Weight

These studies showed that the structure of coal is flexible so as to hold solvent molecules between its molecules. In fact, this flexibility of intra and intermolecular bondings in coal molecules renders further extractable the residual coal obtained after AO extraction, in solvents such as Qn, EDA or LP. High boiling solvents such as LP (boiling range 330-350°C) are capable of energizing and stretching the coal macromolecules to such limits that these molecules are disintegrated and thus, reorient and repolymerize after extraction.

Flexibility of coal structure and mobility of loosened molecules is responsible for the successive extraction of coal in solvents having different chemical characteristics. In fact, coal has a heterogeneous structure having different structural units i.e., polyaromatic, hydroaromatic and paraffinic units linked through C-C, C-N-C, C-O-C and C-S-C linkages. The solvents having structural similarities with the structural units present in coal can easily dissociate and mobilize the coal molecules for their solution in that solvent. The extent of similarity between the structures of coal and that of the solvent and the boiling point of the solvent were generally found to determine the extent of extractability of coal.

The swelling ratio in Qn of the residual coal obtained after AO extraction was found to be more than that of the original coal (1). This showed that AO extraction results in reducing the degree of cross-linking in the structure of coal. However, extraction of coal in EDA or LP was found to result in an increase in the degree of cross-linking in the structure of coal, as revealed by the swelling studies. Probably, entrapment of EDA in coal would have resulted in the increase in the cross-linking in the structure of coal. LP extraction, being a high temperature extraction in a nonreactive and less interactive solvent, would result in the residual coal having a repolymerized cross-linked structure. The IR spectral studies of the residual coal obtained after the extraction of coal in AO or EDA or LP were found to show an increase in the aromatic character and a decrease in aliphatic character. The absorptions due to C=O group were missing in all the extracted coal residues obtained using AO or EDA or LP as a solvent. The percentage carbon and the atomic H/C ratios of the residual coals obtained after extraction in different solvents were also found to have been decreased in

comparison to those of the starting coal. This showed that coal might have undergone depolymerization, degradation and dehydrogenation as a result of extraction in AO, EDA or LP.

If the extraction results obtained after successive extraction in AO-EDA-LP solvents are analyzed then it can be seen that each solvent can extract its share of coal products that is structural moieties from coal which resemble its structure or properties. In fact, each solvent would extract the coal and would chemically depolymerize or degrade the coal for rendering it extractable in the next solvent of the successive extraction sequence to allow the extraction of increased amount of coal. The depolymerizing, degrading and molecular dispersing or dissociating ability of AO and EDA was found to be more than that of LP. In fact, preextraction with LP had an adverse effect on the successive extraction in AO or in Qn (1) or in EDA.

The point or position of attack i.e. chemical depolymerization or physical dissociation or dispersion of coal, by different solvents can be different depending upon the bond strength or the particular structural similarities between the coal and the solvent and of course, depending on boiling point of the solvent. Anthracene oil was found to be a wonder solvent for extraction of coal and for depolymerizing the coal (both chemically and physically) to render the enhanced amount of the (AO treated) residual coal in the next solvent, i.e., EDA, QN or LP. Orchin et al. (2) have reported the extraction studies on coals using different polynuclear aromatic compound such as phenanthrene, carbazole, pyrene, anthracene, fluoranthene, phenanthridine, fluorene, and diphenyl, etc. The actual three dimensional shape and size of the solvent molecule (especially angular arrangement of condensed aromatic rings instead of linear) were reported to be important factors for the ability of solvents to dissolve and disperse coal. Similarity of coal structure with angular ring phenanthrene type molecules (present in AO) allows the free passage (inside and outside) to these molecules inside the solid coal. This similarity of structures also helps in breaking the coal-coal (molecular) physical interactions such as London, vander Waals forces and H-bondings, by the solvents such as AO.

Since the coal structure is heterogeneous, therefore, a successive multiple solvent attack has been found to be a good way to loosen, unleash, unlock inter and intramolecular forces and disperse and to physically and chemically depolymerize the three-dimensional cross-linked gel structure of coal macromolecules for getting enhanced extraction without using any high pressure technique involving hydrogenation at elevated temperatures. Successive solvolytic extraction of coal affords a convenient and cost effective technique for solvent refining of coal under ambient pressure conditions.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research, New Delhi, India for financial support.

References

1. Sharma, D.K. and Mishra, S., Energy and Fuels, **3**, 641 (1989).
2. Orchin, M., Golumbic, C., Anderson, J.E., and Storch, H.H., Bulletin 505, Bureau of Mines, United States Govt. Printing Office, Washington 1951.